Variations in the estimation of the contribution of environmental tobacco smoke (ETS) to respirable (≤5 μm) indoor air particulates obtained by the use of different analytical methods

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Several methods are in use for the identification of the contribution of particulate associated environmental tobacco smoke (ETS) and sidestream smoke to an atmosphere. These include the measurement of respirable suspended particulates (RSP), measurements of the total UV absorption and total fluorescence emission of a methanol extract of collected particulates and the use of specific marker compounds such as solanesol and scopoletin. Use of these methods gave values for the contribution of particulate ETS to total respirable (≤5 μm) particulates in the ranges 8.3–124.7% for smokers' houses and 9.6–121.2% for smokers' offices, respectively. However, using what we consider to be the most reliable methodology, based on the measurement of solanesol, the average contribution of particulate ETS to total respirable (≤5 μm) particulates for smokers' houses was 21.7% and for smokers' offices was 23.3%.

Aims of investigation

Environmental tobacco smoke (ETS) is a highly complex mixture of compounds that are released through the combustion (oxidation or pyrolysis) of tobacco leaves. The measurement of tobacco associated emissions has been widely researched and hundreds of compounds have been identified in the emissions (both vapour and particulate associated) released through smoking.[1]

Early methods for the identification of tobacco smoke used the total respirable suspended particulate (RSP) value.[2,3] The quantity of particulate material sampled on a filter paper at a certain flow for a period of time produces a mass value of particulates per cubic volume (often a metre) of air. Elevated RSP values are obtained from houses where a smoker is an inhabitant.[4] However, not all particulate material sampled in a smoker's environment is due to ETS. Therefore, the values obtained are always overestimates of the actual contribution of ETS.[3] Indeed, it has been suggested that this overestimation could be as high as 50%.[2]

To reduce this overestimation, more specific methods have been introduced. These include total UV absorption[5] (UVPM) and total fluorescence emission measurements[6] (FPM) of a methanol extract from a sampled particulate filter sample. Both methods have been shown to be more specific than total RSP. However, a value is obtained even when there is no ETS present, suggesting that these methods also overestimate the contribution of ETS to any environment. Therefore, to accurately measure the contribution of ETS in an atmospheric sample, a tracer compound specific to tobacco smoke is required.

The National Academy of Sciences[7] has listed the requirements for such a tracer: (i) the compound should be unique, or nearly unique, to ETS, *i.e.* there is a low contribution of species from other sources; (ii) there should be a determination method available for the species even for low level measurements; (iii) there should be a similar emission factor for the marker from various cigarette products; (iv) the marker should be present in constant proportion to the ETS components that cause adverse health effects.

The identification of a tracer compound is complicated by the fact that both volatile and non-volatile compounds are released in ETS. Some compounds are therefore found in the gaseous phase, some are found associated with particulate material and others are distributed between these two phases.

The ageing of ETS further complicates the accurate determination of the ETS contribution to an atmosphere, as the distribution and concentration of compounds (especially volatiles) can vary quite significantly in a short period of time.[8] Major factors identified as occurring during the ageing of ETS include: (i) coagulation of particulate material, causing a change in the size distribution of particles in ETS;[2,9,10] (ii) variation in the distribution of semi-volatile compounds between the gaseous phase and particulate associated phase;[2,11] (iii) the possibility of reactions between other available chemicals or radiation inducing chemical reactions that degrade compounds in various phases;[11,12] (iv) variation in chemical composition due to recirculation and dilution with outdoor air.[2,13]

Many specific tracer molecules have been identified in ETS. These include nicotine,[9] together with several similar molecules, such as cotinine, nicotyrine or myosmine[9] and 3-ethenylpyridine.[14–16] All of these tracers can be used to identify the contribution ETS has on the gaseous phase of the environment, since they are found almost entirely in the gaseous phase. Tracer compounds that are less volatile and identify the contribution of ETS associated with particulate material include solanesol[12,17] and scopoletin.[18] The use of cadmium has also been suggested as a possible tracer for particulate associated ETS.[19]

Solanesol (3,7,11,15,19,23,27,31,35-nonamethyl-2,6,10,14,18,22,26,30,34-hexatriacontanonaen-1-ol) was the first and most widely used tracer molecule for particulate ETS. It was originally detected in flue cured tobacco in 1956[20] and was initially misidentified as a primary terpenoid alcohol. The compound was later correctly assigned a trisesquiterpenoid

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Curt,
Will you please give this to Raymond L? It addresses the issue of the influence of ETS on outdoor air (cf. Cal.) (p.300).
B Davis

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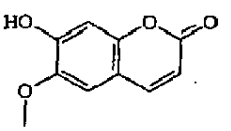
long chain (C45) structure (CH_3–$C(CH_3)CH$–$[CH_2$–CH_2–$C(CH_3)CH]_8$–CH_2–OH).[21] Solanesol has been regularly studied in tobacco leaves,[22,23] but was only recently identified as being present in ETS.[26] Due to its high molecular weight, solanesol is very involatile and is found entirely associated with the particulate emissions of ETS.[27] Solanesol is in fact found in many plants from the Solanaceae family, one member of which is the *Nicotiana* genus. Other members of the family known to contain solanesol include tomato plants, potato plants, eggplants and pepper plants. Therefore, sources other than ETS for solanesol include certain cooking emissions. However, the interference obtained from these in ETS determinations is thought to be of only minor consequence.[26]

The original analytical method for solanesol using GC was complicated by the interference of solanesenes, produced from the pyrolysis of solanesol and solanesyl esters during smoking. The breakdown of solanesol at high temperatures in the GC oven also hindered the direct quantification of solanesol by GC analysis.[27] However, by derivatizing the alcohol group with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), analysis was possible.[14,27] A limitation of this method is that the extraction and sample manipulation methods are time consuming and specific only to solanesol determination.[26] Another limitation of this methodology as reported was that the performance of the chromatographic column rapidly degraded.[26] This is a major limitation in the use of GC for the determination of solanesol and hence it was not used in this study.

An HPLC method for the determination of solanesol, using UV detection at $\lambda = 205$ nm of the methanolic extract of a particulate filter sample, has been developed.[27] The methanol extract can also be used to measure UVPM and FPM values for the determination of ETS in a sample. A slightly modified version of this method has been used for the solanesol determinations in this study (see 'Experimental').

Another compound that has been identified as a possible particulate associated ETS tracer molecule is scopoletin (6-methoxy-7-hydroxy-coumarin) (see structure).[28] This compound has been identified in tobacco leaves[29,30] and has also recently been quantitatively determined in particulate ETS.[18]



Scopoletin is extracted into methanol from particulate material collected on Teflon impregnated glass fibre filters. Quantitative analysis can be achieved using reverse phase HPLC and fluorescence detection (excitation, 342 nm; emission, 464 nm[18]). A slight variation of this published method was used for the scopoletin determinations carried out in this study (see 'Experimental').

Long chain iso- (2-methyl) and anteiso-alkanes (3-methyl) (C29–C34) have also been used to identify the contribution of ETS particulate material to an outdoor environment in Los Angeles.[31] These marker compounds were not investigated further as the four previously described particulate methods seemed sufficient to quantify ETS particulate contributions in both indoor and outdoor air.

In this study, we report the determination of UVPM, FPM, solanesol and scopoletin, together with RSP, for samples of ETS collected in a controlled smoking environment. Quantification ratios have been calculated from the control data for 'pure ETS particulates' for use in the calculation of the contribution of particulate ETS to total respirable particulates in field samples. Field samples have been collected from a range of smoking and non-smoking environments. The values for the contribution of ETS to airborne particulate levels in these samples, obtained using each of the methods, are critically compared.

Experimental

Sampling

Controlled sidestream smoke samples. Controlled sidestream smoke sampling was kindly undertaken by Rothmans International at their research and development facility in Basildon, Essex.

Each cigarette was 'smoked by a Borgwaldt' smoking machine (complying with the international standard ISO 3308). The smoking machine was situated in a smoke generation room attached to the main sampling room.[32] Mainstream smoke was trapped on a Cambridge filter and the mainstream vapour emissions were piped directly out of the smoke generation system.

The external smoke generation chamber was 0.7 m wide, 0.849 m long and 0.795 m high, producing a volume of 0.472 m^3. Access to the smoking machine positioned within was achieved through a hinged door. Rubber gaskets ensured an airtight seal around the door edge. An electric cigarette lighter penetrated through the door *via* an airtight slip ring gasket that enabled ignition of the cigarettes while maintaining a closed atmosphere. Fresh sidestream smoke (which is the emission directly from the burning cigarette tip: ETS also contains exhaled mainstream smoke from a smoker) was transferred from the smoke generation chamber to the main room *via* an interconnecting duct. This was achieved with the use of the recirculation system. This drew air from the main chamber through the base of the smoke generation chamber and back into the mainroom through the interconnecting duct, taking with it the freshly produced sidestream smoke.

Sidestream smoke produced in the smoke generation chamber was circulated into a model room, which was 2.745 m wide, 3.245 m long and 2.3 m high, producing a total volume of 20.78 m^3. The walls were constructed of interlocking panels of heavy duty PVC coated 'galvatite' sheet metal. Three main chamber walls were hollow, including a serpentine void in which thermostatted air was recirculated *via* a temperature control/fan unit positioned in the roof. Insulation of the room kept the temperature constant at 21 °C. The room floor was constructed of a composite material of PVC, glass fibre and aluminium oxide bonded to the concrete floor. Samples were taken directly from this room using sampling equipment or *via* sampling ports positioned in the door.

Particulate samples. Particulate material was sampled onto a 37 mm Teflon impregnated glass fibre filter paper (Gelman Science, Supelco, Poole, Dorset, UK) in a round 'impaction target' type filter holder. The size of particulate material sampled could be determined by the flow through the sampling system. The 'target' type filter head used the principle that larger particles hit and stuck to the target placed adjacent to the sampling orifice, while smaller particulate material was swept around the target and sampled on the filter paper (pore size, 1 μm) situated directly behind the target. Directly behind the filter head was an XAD-4 resin tube to collect any organic compounds found in the gaseous phase. (These results are not discussed in this paper.) The total flow through this sampling apparatus was 1 l min^{-1}, achieved by a personal sampling pump (SKC Ltd, Dorset, UK). The particulate material sampled at this flow was ≤5 μm.

Immediately after sampling, all tubes were separated, labelled and capped, while all filter samples were weighed and stored in amber screw topped vials. All samples were stored in a fridge (<5 °C) prior to pre-treatment and analysis.

Sites sampled

After examining previous studies, it was decided that the following types and numbers of sites would be investigated

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with a sampling system for both indoor and outdoor environments: (i) five smokers' homes; (ii) four non-smokers' houses; (iii) four smokers' offices; (iv) four non-smokers' offices.

Other types of outdoor sites were also used: (v) eight roadside sites within the city of Sheffield; (vi) two sites in the countryside outside of the city of Sheffield.

All the houses were situated in residential areas around the city of Sheffield. Samples were taken from houses during either a Saturday or Sunday when the occupants were present in the house and emissions due to the presence of people were at their highest. All the office samples were taken from one building situated in the city centre of Sheffield. The samples were taken during the week so that the occupants would once again be present in the office for the maximum amount of time. By taking both indoor and outdoor samples from the various houses/offices, diffusion of sources from one context to the other could also be investigated.

Roadside samples were either taken from the city centre (adjacent to a large bus and train station), or along major roads that radiated from the city centre. Countryside samples were obtained from areas of the Peak District, away from roads, in an attempt to obtain 'control' samples.

Indoor sampling devices were housed in a briefcase to reduce the noise of the pumps and prevent tampering once the system was installed. The outside sampling apparatus was housed in a wooden box designed to look like a large bird box, which could be attached to the side of a building. The box was lockable to prevent tampering and vandalism during the sampling period.

Determination of respirable particulate material ($\leqslant 5$ μm)

A Perkin-Elmer PU-50 balance was used to measure the mass of the 37 mm Teflon impregnated glass fibre filter (Gelman Science, Supelco, Poole, Dorset, UK) prior to and after sampling. The balance was calibrated prior to use with NAMAS (National Accreditation of Measurement and Sampling) accredited weights. Accuracy at low mass levels can be affected quite markedly by static electricity. Such effects were minimized by placing the filter in front of an antistatic fan for a few seconds and repeated weighings until three consecutive values within 3 μg were obtained. An average of the three values was then used as the actual mass of the filter.

Extraction

Each filter was cut in half using a ceramic gas chromatography column cutter in order to prevent as much elemental contamination as possible.

One half of the filter was placed in a 7 ml amber screw topped vial and methanol (5 ml) was added. (The other half of the filter was used for elemental analysis, and is not discussed in this paper.) The vial was then heated to 50 °C in an oven for 30 min. This methanol extract was used for the following four analytical procedures.

Determination of total UV absorption (UVPM)

All analyses were carried out using a Pye Unicam PU 4015 isocratic HPLC pump with a Pye Unicam PU 4025 UV detector operating at 325 nm.[33] A 7125 Rheodyne injector with a 50 μl loop was used for all the manual injections. A Hewlett Packard HP3394 integrator was used to obtain the relevant integrated chromatograms. Methanol was used as the eluent, at a flow rate of 0.4 ml min^{-1}, with no column used for analytical separation. 2,2',4,4'-Tetrahydroxybenzophenone (Aldrich, Poole, Dorset, UK) was used as an external calibration molecule against which the concentration of the total UV measurement was taken.[5,33] A calibration graph of 0.05–10 ppm was completed to ensure linearity over this range.

Determination of total fluorescence (FPM)

The HPLC system consisted of a Jasco LG-980-02 tertiary gradient pump, with a Jasco PU-980 intelligent HPLC unit. Injections were performed manually using a 7125 Rheodyne injector, with a 20 μl injection loop. The eluent used was 100% methanol, at a flow rate of 0.5 ml min^{-1}. Detection was by a Jasco FP-920 intelligent fluorescence detector, $\lambda_{ex} = 300$ nm, $\lambda_{em} = 420$ nm.[33] No column was used for total fluorescence determination. Integration was by a Shimadzu C-R4A chromatopac computing integrator. Scopoletin was used as an external calibration molecule against which total fluorescence was measured.

Determination of solanesol

The pump and detector were the same as those described in the UV section above. The wavelength used for the analysis was 210 nm.[33] A 7125 Rheodyne injector with a 200 μl loop was used for all the manual injections. A Spherisorb ODS (5 cm × 4.6 mm) column was used with 100% methanol at 1 ml min^{-1}. An external calibration graph of solanesol (Aldrich, Poole, Dorset, UK) was used to quantify the solanesol in all the samples analysed.

Determination of scopoletin

The HPLC and integration system were the same as that described in the total fluorescence section above. All manual injections were completed using a 7125 Rheodyne injector, with a 20 μl injection loop. The analytical column used was a Spherisorb ODS (25 cm × 4.6 mm) with an eluent system of 90% water–10% methanol held for 5 min, followed by a 15 min ramp to 100% methanol, which was held for 15 min. The flow rate of the eluent was 1 ml min^{-1}. Detection was by a Jasco FP-920 intelligent fluorescence detector, $\lambda_{ex} = 300$ nm, $\lambda_{em} = 420$ nm.[33] Scopoletin was used as an external calibration molecule.

Results and discussion

Respirable suspended particulates (RSP) ($\leqslant 5$ μm)

The range and mean mass of RSP ($\leqslant 5$ μm) collected can be seen in Table 1. The colour of the filter was also noted for each sample. Filter samples taken from houses/offices in which smoking had occurred often exhibited an orange/brown colouration, while samples taken from non-smokers' houses/offices or outdoor samples were grey in colour.

It can be seen from Table 1 that the smokers' houses contained the highest average quantity of RSP ($\leqslant 5$ μm), with a mean value of above 106 μg m^{-3} (range, 42.6–212 μg m^{-3}). Smokers' office values were also fairly high, with an average value of 63.3 μg m^{-3} (range, 39.8–93.5 μg m^{-3}), identifying ETS as a source of RSP ($\leqslant 5$ μm). However, non-smokers' house average values were not far from this office value, with an average of around 57.7 μg m^{-3} (range, 21.8–124.1 μg m^{-3}). It should be noted, however, that this value is high due to the occupants of one of the non-smokers' houses (house 2) burning incense during the sampling period causing an increase in particulate material and producing a faint orange colour on the filter paper.

The mean values from this study (106.1 μg m^{-3} and 57.7 μg m^{-3} for smokers' and non-smokers' houses, respectively) are slightly higher than the RSP levels in different indoor contexts previously reported. Levels of 88.81 μg m^{-3},[34] 74 μg m^{-3},[4] 44.6 μg m^{-3}[35] and 44.1 μg m^{-3}[36] have been reported for smokers' homes and 27.6 μg m^{-3},[34] 28 μg m^{-3},[4] 18.1 μg m^{-3}[35] and 15.2 μg m^{-3}[36] for non-smokers' homes. Our slightly higher values are as expected, since the literature values were obtained using personal samples while our study

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Table 1 The range and mean concentration ($\mu g\ m^{-3}$) of ETS associated material in different sampling environments determined by measurement of total respirable suspended particulates [RSP ($\leqslant 5\ \mu m$)], total UV absorbance (UVPM), total fluorescence (FPM) and solanesol and scopoletin[a]

	RSP ($\leqslant 5\ \mu m$)		UVPM		FPM		Solanesol		Scopoletin	
Indoor	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Non-smokers' house	21.8–124.1	57.7	0.44–1.66	1.02	0.13–1.0	0.39	N.D.[b]	N.D.	N.D.	N.D.
Smokers' house	42.6–212	106.1	5.78–50.8	17.4	0.38–6.20	2.06	0.30–3.90	1.12	0.01–0.29	0.11
Non-smokers' office	21.8–56.5	32.1	0.58–2.42	1.49	0.06–0.29	0.16	N.D.	N.D.	N.D.	N.D.
Smokers' office	39.8–93.5	63.3	3.10–18.0	9.27	0.49–3.43	1.61	0.15–0.98	0.59	0.04–0.08	0.06
Roadside	N/A[c]	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Countryside	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

	RSP		UVPM		FPM		Solanesol		Scopoletin	
Outdoor	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Non-smokers' house	18.5–44	31.3	0.07–1.39	0.78	0.15–0.51	0.3	N.D.	N.D.	N.D.	N.D.
Smokers' house	26.4–78	43.8	1.16–5.12	2.56	0.01–0.15	0.09	N.D.	N.D.	N.D.	N.D.
Non-smokers' office	25–69	40.4	0.99–1.97	1.69	0.09–0.46	0.24	N.D.	N.D.	N.D.	N.D.
Smokers' office	14.1–33.3	22.7	0.66–2.74	2.04	0.09–0.79	0.28	N.D.	N.D.	N.D.	N.D.
Roadside	9.7–50.7	31.9	1.15–3.70	2.04	0.05–1.04	0.3	N.D.	N.D.	N.D.	N.D.
Countryside	47–59.3	53.1	1.23–1.74	1.49	0.03–0.21	0.12	N.D.	N.D.	N.D.	N.D.

[a]No standard deviation value is shown as each site is individual. The standard deviation value can therefore be higher than the mean value which is calculated to visually identify contextual differences. [b]N.D., not detected. [c]N/A, not applicable (there are no indoor roadside or countryside sample contexts).

used static sampling. This will cause increases in concentration due to the samplers being constantly exposed to ETS.

All the other sites, including all outdoor contexts, have a similar average RSP value of between 22.7 $\mu g\ m^{-3}$ (outside the smokers' offices) and 53.1 $\mu g\ m^{-3}$ (in the countryside). The presence of a cat as a pet in one of the non-smokers' houses appears to have had little effect on the particulate mass. RSP ($\leqslant 5\ \mu m$) can therefore be seen to be fairly ubiquitous throughout the environment, with elevated levels being most prominent in indoor environments in which smoking has occurred. However, other sources can also produce elevated quantities of particulate material as seen in non-smokers' houses and also the countryside samples (possibly pollen).

The contribution of ETS to particulate material in an atmosphere was initially measured using the quantity of RSP determined in a sample.[3,4] However, the results obtained in this study for RSP show that such particulate material is found ubiquitously. This is also apparent in other publications from field studies.[34,37] The use of RSP values would therefore appear to clearly overestimate the contribution of ETS to an atmosphere.

Total UV absorbance (UVPM)

The mean UVPM values obtained in this study for each context can be seen in Table 1. These data clearly show that the sites in which smoking has taken place give higher average concentrations of UVPM and also much wider ranges. The average concentrations of UVPM in the two indoor smoking contexts are 17.4 $\mu g\ m^{-3}$ and 9.3 $\mu g\ m^{-3}$ for houses and offices, respectively. The next highest mean UVPM value in all the other contexts is 2.56 $\mu g\ m^{-3}$, which is the outdoor sample of smokers' houses. This difference in UVPM concentration in the smoking/non-smoking contexts compares favourably with published data.[34,38] In these reports, higher concentrations are also seen in smoking contexts. However, the data in Table 1 show that there is always a response for UVPM in all sample contexts (this can also be seen in the literature[34,39]). This demonstrates that the UVPM method is not specific to ETS and that again overestimation is inevitable.[39]

Total fluorescence emission (FPM)

UVPM has largely been superseded by the use of FPM for ETS particulate quantification.[40] The average concentration for FPM can be seen in Table 1 for all sampled contexts. It can be seen from these data that the average FPM values are higher in the smokers' indoor samples, with smokers' houses and smokers' offices giving values of 2.06 $\mu g\ m^{-3}$ and 1.61 $\mu g\ m^{-3}$, respectively. These results are similar to those published in the literature,[34] although those samples were from personal monitors. However, once again it can be seen that there is an FPM value obtained from all the sites. The highest mean concentration (after smokers' samples) is from the indoor non-smokers' houses at 0.39 $\mu g\ m^{-3}$ with a positive reading obtained from every sample. This once again indicates that the FPM method is not specific to ETS measurements, and hence will overestimate the contribution of ETS.

Solanesol determinations

Solanesol was determined in all the field samples and the data are shown in Table 1. These data clearly indicate that solanesol was found only in sites where smoking had occurred, with mean concentrations of 1.12 $\mu g\ m^{-3}$ and 0.59 $\mu g\ m^{-3}$ in smokers' houses and offices, respectively. No evidence of ETS material diffusing into the equivalent outdoor context was identified, as solanesol was not detected in measurable quantities in any outdoor sample. This suggests that solanesol is an excellent marker for ETS. It is also well known that solanesol is stable in the atmosphere when attached to ETS particulate material.[8,41]

Scopoletin determinations

The concentrations of scopoletin determined in all the field samples can be seen in Table 1. These data show that scopoletin was found only in sample sites where smoking had taken place. Mean concentrations of 112.5 $ng\ m^{-3}$ and 56.5 $ng\ m^{-3}$ were obtained in smokers' houses and offices, respectively. As with solanesol, no scopoletin was identified in any outdoor sample, providing evidence of no major diffusion of ETS material to an adjacent outdoor context. Hence, scopoletin also seems to be an ideal marker compound for ETS.

Calculation of the percentage contribution of particulates from ETS to total airborne particulate material

The measurement of UVPM, FPM, solanesol and scopoletin associated with a gram of 'pure' particulate ETS has been reported in the literature.[41] These values can be used to

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Table 2 ETS quantification ratios determined in this study and by Severson *et al.*[23] These values are used to determine the percentage contribution of ETS to total particulates from measurements of 'pure' ETS particulates, e.g. if 100 μg of 'pure' particulate ETS contains 5 μg of scopoletin, then the quantification ratio is 20

Method	Ratio	Published ratio[23]
UVPM	5.3	8.2
FPM	28.7	45
Solanesol	53.7	42
Scopoletin	203.0	—

determine the quantity of sampled particulate material that has been released by ETS by the calculation of the appropriate quantification ratio, *e.g.* if 100 μg of 'pure' particulate ETS contains 5 μg of scopoletin, then the quantification ratio is 20. The ratios calculated from the controlled smoking experiments are shown in Table 2 together with those ratios previously reported.[19] These compare favourably with the ratios obtained during our research on Rothmans' cigarettes, which are also very similar to the ratios obtained independently by Rothmans International.[42] Variation between the two sets of ratios occurs because the samples were taken from slightly different standard smoking environments. The published data[21] sampled an ETS atmosphere from people smoking in a closed environment, while the samples taken at Rothmans International came from a closed environment in which a smoking machine was used to produce sidestream smoke. It has been noted previously that a variation in ratios is obtained when these different methods of standard tobacco smoke formation are used.[42]

Using our calculated quantification ratios, the percentage contribution of ETS to a particulate sample was calculated by the following method:

$$\%\,\text{contribution} = (A/B) \times 100$$

where A is the particulate material ($\mu g\,m^{-3}$) attributable to ETS [method or compound value measured in field sample ($\mu g\,m^{-3}$) × quantification ratio] and B is the total particulate material in the field sample ($\mu g\,m^{-3}$).

The percentage contribution of ETS to total particulates for each sample site, calculated using the data obtained from each of the four methods of analysis, is shown in Table 3.

The use of UVPM leads to high average percentage ETS values being calculated for the two indoor smoking environments: 67.3% and 71.3% of the total particulates were calculated as attributable to ETS in smokers' houses and offices, respectively. Outdoor samples of smokers' offices gave values of 51.6%, and in fact all other sample sites including non-smokers' and rural sites gave a value for the ETS contribution to total particulates of above 10%. Two of the samples (smokers' house 4 and smokers' office 4) gave a contribution to particulates from ETS of above 100% (124.7% and 121.2%, respectively). These data would appear to clearly indicate that an overestimation for the contribution of ETS is obtained using this method.

Data published by Phillips *et al.*[39] also suggest that UVPM overestimates the percentage ETS contribution, since the use of more specific marker compounds (solanesol and scopoletin) reported in the same publication gave lower values. Values for the mean percentage contribution from ETS from UVPM measurements given in the literature are 44.9% and 39.5% in smokers' homes and smokers' work environments, respectively.[34] These values are lower than those indicated by our work. However, this is as expected since the samples in the literature[34] were from personal monitors, whilst our work is based on static room sampling as discussed earlier.

The values for the ETS contribution calculated using FPM measurements are shown in Table 3. The average percentage contributions calculated for the two smoking environments are lower than those identified by UVPM [smokers' houses 40.94% (FPM) compared to 67.3% (UVPM) and smokers' offices 62.1% (FPM) compared to 71.3% (UVPM)]. This shows that, on average, FPM is a more specific method for the measurement of the ETS particulate contribution compared to UVPM. In the literature, the percentages of ETS particulate material in total particulates, calculated from FPM measurements (using personal samplers), were 39.3% and 34.0% for smokers' houses and offices, respectively.[34] These are lower than the median values calculated from UVPM measurements given in the same paper, again suggesting an improvement in specificity.

The percentage contributions of ETS to total particulates calculated by the measurement of solanesol were 21.7% and 23.3% for smokers' houses and offices, respectively (Table 3). These results are very similar to the previously published values of 31.3% and 27.2% for smokers' houses and offices, respectively[34] (personal sampling was undertaken in that study). These average contributions for ETS particulate material are far lower than those determined by the UVPM and FPM methods, clearly suggesting that solanesol is more specific to ETS.

The percentage ETS contributions to total particulates calculated for the smokers' house samples using solanesol

Table 3 Comparison of the values for the percentage contribution of ETS to total respirable suspended particulates [RSP (≤5 μm)], calculated from the measurement of the total UV absorbance (UVPM) and total fluorescence (FPM) and the determination of solanesol and scopoletin

	UVPM		FPM		Solanesol		Scopoletin	
Indoor	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Non-smokers' house	4.54–19.0	11.29	7.9–34.1	18.84	0	0	0	0
Smokers' house	33.6–124.7	67.3	17.3–82.5	40.94	5.89–49.0	21.7	1.9–19.1	8.3
Non-smokers' office	14.4–53.3	27.9	7.3–22.8	14.0	0	0	0	0
Smokers' office	42.2–121.16	71.3	36.0–100.8	62.1	10.6–28.0	23.3	6.9–12.6	9.6
Roadside	N/A[a]	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Countryside	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	UVPM		FPM		Solanesol		Scopoletin	
Outdoor	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Non-smokers' house	1.6–19.8	11.5	10.8–66.5	30.6	0	0	0	0
Smokers' house	11.4–58.6	29.5	0.26–9.1	5.31	0	0	0	0
Non-smokers' office	12.8–42.6	26.6	10–40	18.1	0	0	0	0
Smokers' office	7.4–79.7	51.6	7.3–92.7	33.6	0	0	0	0
Roadside	18.4–77.7	39.2	3.2–103.5	29.2	0	0	0	0
Countryside	14.4–14.5	14.5	1.29–13.0	7.1	0	0	0	0

[a]N/A, not applicable.

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Table 4 Overestimation of the percentage contribution of ETS to total respirable suspended particulates [RSP ($\leqslant 5$ μm)], obtained from calculations based on the measurement of total UV (UVPM) and total fluorescence (FPM) in comparison to the use of solanesol determinations

Site	UVPM (%)	FPM (%)
Non-smokers' house (in)	11.3	18.9
Non-smokers' house (out)	11.5	30.6
Smokers' house (in)	45.6	19.2
Smokers' house (out)	29.5	5.31
Non-smokers' office (in)	27.9	14.0
Non-smokers' office (out)	24.6	16.1
Smokers' office (in)	48.0	38.8
Smokers' office (out)	51.6	33.6
Roadside	39.2	29.2
Countryside	14.5	7.13

measurements vary quite considerably, ranging from 5.89% to 49.0%. These variations are due to differences in room size, ventilation, the number of cigarettes smoked during the sampling period and the distance from the sampler to the smoker (as room samples were taken, not personal samples).

The solanesol measurements carried out in offices give far more consistent values for the ETS contribution to total particulates. This is in part due to the offices sampled being of roughly the same size, with similar ventilation rates, and the fact that a similar number of cigarettes were smoked during the sampling period.

Using the scopoletin measurements, the percentage contribution to total particulate material from ETS was calculated and is shown in Table 3. The average contributions of particulate ETS identified using scopoletin as a marker compound were determined to be 8.32% and 9.59% for smokers' houses and offices, respectively. Compared to the solanesol data, these values are far lower. This indicates either that scopoletin is the most specific marker for ETS or that an underestimation has occurred in this case. An underestimation caused by the instability of scopoletin when exposed to UV radiation is thought to be the most likely explanation. Another likely contribution to the underestimation is an error in the quantification ratio obtained from the controlled smoking experiments. The samples were taken over a short period of time after a number of cigarettes had been rapidly smoked by the smoking machine. This sample would therefore be expected to contain a larger amount of scopoletin, in comparison to field samples (which were collected over 12 h), as it had little time to 'age'.

Overall, the results obtained in this study appear to agree with the trends in the absolute concentrations and percentage contributions reported in the literature. Hence, it can be seen that simple extrapolation of RSP ($\leqslant 5$ μm) data would appear to grossly overestimate the contribution of ETS to an indoor atmosphere. UVPM and FPM measurements reduce this overestimation to some extent, but must still lead to an overestimation since values were found for all samples in all contexts. Table 4 summarizes the average overestimation of ETS from determinations carried out by UVPM and FPM measurements. These values were calculated by making the assumption that the data obtained from solanesol measurements are the most reliable. This assumption is based on literature reports and the observation reported here that solanesol was only found in smoking environments.

ETS particulates in outdoor air masses

In order to investigate the effect of ETS particulates on outdoor air masses, the outdoor sampling was undertaken (Table 3). It can be seen that the non-specific methods identified a contribution from ETS to total particulates for all of the outdoor samples taken. However, as previously discussed, from the indoor data, we consider that the measurement of solanesol leads to the most accurate estimations of ETS. Solanesol was not present in detectable quantities in any of the outdoor air samples. This suggests that the contribution of ETS to outdoor air quality is negligible.

Conclusions

Use of the various methods gave values for the average contribution of particulate ETS to total respirable ($\leqslant 5$ μm) particulates of 8.3–124.7% for smokers' houses and 9.59–121.2% for smokers' offices. However, using what we consider to be the most reliable methodology, based on the measurement of solanesol, the average contribution of particulate ETS to total respirable ($\leqslant 5$ μm) particulates for smokers' houses was 21.7% and for smokers' offices was 23.3%.

Use of the non-specific methods (RSP, UVPM and FPM) gave values for the average contribution of particulate ETS to total respirable ($\leqslant 5$ μm) particulates of 4.54–34.1% for non-smokers' houses and 7.31–53.3% for non-smokers' offices. In these cases, use of the specific marker compound solanesol was not detected in either context.

It can therefore be concluded that the use of non-specific analytical methods, including the measurement of RSP, UVPM and FPM, leads to an overestimation of the contribution of ETS to total indoor particulates. Use of such methods can also lead to the conclusion that ETS is a significant contributor to outdoor air particulate concentrations. This is not supported by the use of data based on measurement of a specific marker compound.

Of the marker compounds tested, solanesol gives the most reliable results since scopoletin appears to degrade on sample filters leading to an underestimation of ETS. However, the stability of solanesol when adsorbed to particulate material has not been thoroughly examined and requires further investigation before it can be suggested as the definitive marker compound for ETS.

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References

1 B. P. Leaderer, *Risk Anal.*, 1990, **10**, 19.
2 D. J. Eatough, in *Modelling of Indoor Air Exposure*, ed. N. L. Nagada, American Society for Testing and Materials, Philadelphia, PA, 1993, pp. 42–63.
3 J. L. Repace and A. H. Lowrey, *Science*, 1980, **208**, 464.
4 J. D. Spengler, R. D. Treltman, T. D. Tosteson, D. T. Mage and M. L. Soczek, *Environ. Sci. Technol.*, 1985, **19**, 700.
5 J. M. Conner, G. B. Oldaker III and J. J. Murphy, *Environ. Technol.*, 1990, **11**, 189.
6 M. R. Guerin, R. A. Jenkins and B. A. Tomkins, *The Chemistry of Tobacco Smoke: Composition and Measurement*, Lewis Publishers Inc., Chelsea, MI, 1992.
7 National Academy of Sciences Report, *Environmental Tobacco Smoke, Measuring Exposure and Health Effects*, GPO, Washington, DC, 1986.
8 G. B. Neurath, S. Petersen, M. Dünger, D. Orth and F. G. Pein, *Environ. Technol.*, 1991, **12**, 581.
9 C. L. Benner, J. M. Bayona, F. M. Caka, H. Tang, L. Lewis, J. Crawford, J. D. Lamb, M. L. Lee, E. A. Lewis, L. D. Hansen and D. J. Eatough, *Environ. Sci. Technol.*, 1989, **23**, 688.
10 L. Morawska, M. Jamriska and N. D. Bofinger, *Sci. Total Environ.*, 1997, **196**, 43.
11 D. J. Eatough, C. L. Benner, J. M. Bayona, G. Richards, J. D. Lamb, M. L. Lee, E. A. Lewis and L. D. Hansen, *Environ. Sci. Technol.*, 1989, **23**, 679.
12 H. Tang, G. Richards, C. L. Benner, J. P. Tuominen, M. L. Lee, E. A. Lewis, L. D. Hansen and D. J. Eatough, *Environ. Sci. Technol.*, 1990, **24**, 848.

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13 C. V. Thompson, R. A. Jenkins and C. E. Higgins, *Environ. Sci. Technol.*, 1989, **23**, 429.
14 D. J. Eatough, C. L. Benner, H. Tang, V. Landon, G. Richards, F. M. Caka, J. Crawford, E. A. Lewis, L. D. Hansen and N. L. Eatough, *Environ Int.*, 1989, **15**, 19.
15 A. T. Hodgson, J. M. Daisey, K. R. R. Mahanama, J. Ten Brinke and L. E. Alevantis, *Environ. Int.*, 1996, **22**, 295.
16 M. W. Ogden, D. L. Heavner, T. L. Foster, K. C. Maiolo, S. L. Cash, J. D. Richardson, P. Martin, P. S. Simmons, F. W. Conrad and P. R. Nelson, *Environ. Technol.*, 1996, **17**, 239.
17 P. R. Nelson, F. W. Conrad, S. P. Kelly, K. C. Maiolo, J. D. Richardson and M. W. Ogden, *Environ. Int.*, 1997, **23**, 47.
18 C. H. Risner, *J. Liq. Chromatogr.*, 1994, **17**, 2723.
19 D. Wu, S. Landsberger and S. M. Larson, *Environ. Sci. Technol.*, 1995, **29**, 2311.
20 R. L. Rowland, P. H. Latimer and J. A. Giles, *J. Am. Chem. Soc.*, 1956, **78**, 4680.
21 R. E. Erickson, C. H. Shunk, N. R. Trenner, B. H. Arison and K. Folkers, *J. Am. Chem. Soc.*, 1959, **81**, 4999.
22 B. H. Woollen and D. H. Jones, *J. Chromatogr.*, 1971, **61**, 180.
23 R. F. Severson, J. J. Ellington, P. F. Schlotzhauer, R. F. Arrendale and A. I. Schepartz, *J. Chromatogr.*, 1977, **139**, 269.
24 R. F. Severson, J. J. Ellington, R. F. Arrendale and M. E. Snook, *J. Chromatogr.*, 1978, **160**, 155.
25 J. B. Wooten, *J. Agric. Food Chem.*, 1985, **33**, 419.
26 M. W. Ogden and K. C. Maiolo, *Environ. Sci. Technol.*, 1989, **23**, 1148.
27 M. W. Ogden and K. C. Maiolo, *LCGC*, 1992, **10**, 459.
28 C. H. Risner, *J. Liq. Chromatogr.*, 1993, **16**, 4117.
29 W. A. Court, *J. Chromatogr.*, 1977, **130**, 287.
30 M. E. Snook and O. T. Chortyk, *Tobacco Sci.*, 1982, **26**, 25.
31 W. F. Rogge, L. M. Hildemann, M. A. Mazurek, G. R. Cass and B. R. T. Simoneit, *Environ. Sci. Technol.*, 1994, **28**, 1375.
32 *Internal Standard ISO 3308*, International Organization for Standardization, Geneva, 3rd edn., 1991.
33 Standard Methods from Rothmans International, 1997, personal communication.
34 D. L. Heavner, W. T. Morgan and M. W. Ogden, *Environ. Int.*, 1996, **22**, 159.
35 R. A. Jenkins, A. Palausky, R. W. Counts, C. K. Bayne, A. B. Dindal and M. R. Guerin, *J. Exp. Anal. Environ. Epidemiol.*, 1996, **6**, 473.
36 B. P. Leaderer and S. K. Hammond, *Environ. Sci. Technol.*, 1991, **25**, 770.
37 K. Phillips, M. C. Bentley, D. A. Howard and G. Alván, *Scand. J. Work Environ. Health*, 1996, **22**, 1.
38 R. A. Jenkins, M. A. Palausky, R. W. Counts, M. R. Guerin, A. B. Dindal and C. K. Bayne, *Lung Cancer*, 1996, **14**, S195.
39 K. Phillips, D. A. Howard, D. Browne and J. M. Lewsley, *Environ. Int.*, 1994, **20**, 693.
40 M. W. Ogden, K. C. Maiolo, G. B. Oldaker and F. W. Conrad, in *Indoor Air 90. Proceedings of the 5th International Conference on Indoor Air Quality and Climate, Ottawa, 1990*, Canada Mortgage and Housing Corp., Ottawa, 1990, vol. 2, pp. 415–420.
41 P. R. Nelson, D. L. Heavner, B. B. Collie, K. C. Maiolo and M. W. Ogden, *Environ. Sci. Technol.*, 1992, **26**, 1909.
42 B. Frost and D. Tuck, Rothmans International, 1997, personal communication.

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